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<p>(21) International Application Number: PCT/EP93/03695</p> <p>(22) International Filing Date: 23 December 1993 (23.12.93)</p> <p>(30) Priority Data:</p> <table> <tr> <td>93300147.1</td> <td>11 January 1993 (11.01.93)</td> <td>EP</td> </tr> <tr> <td colspan="2">(34) Countries for which the regional or international application was filed:</td> <td>GB et al.</td> </tr> <tr> <td>93300180.2</td> <td>13 January 1993 (13.01.93)</td> <td>EP</td> </tr> <tr> <td colspan="2">(34) Countries for which the regional or international application was filed:</td> <td>GB et al.</td> </tr> </table> <p>(71) Applicant (for all designated States except US): QUEST INTERNATIONAL B.V. [NL/NL]; Huizerstraatweg 28, NL-1411 GP Naarden (NL).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): BEHAN, John, Martin [GB/GB]; Shermel, Ball Lane, Kennington, Ashford, Kent TN23 1AA (GB). BIRCH, Richard, Arthur [GB/GB]; 38 Martello Drive, Hythe, Kent CT21 6PJ (GB). LEAKE, John [GB/GB]; 116 Oldfield Drive, Chester, Cheshire CH3 5LW (GB). NESS, Jeremy, Nicholas [GB/GB]; 22 River Court, Chartham, Canterbury, Kent CT4 7JN (GB). NOCK, Anthony [GB/GB]; 61 Aviemore Drive, Fearnhead, Warrington, Cheshire WA2 9TQ (GB). PERRING, Keith,</p>		93300147.1	11 January 1993 (11.01.93)	EP	(34) Countries for which the regional or international application was filed:		GB et al.	93300180.2	13 January 1993 (13.01.93)	EP	(34) Countries for which the regional or international application was filed:		GB et al.	<p>Douglas [GB/GB]; 41 Balmore Park, Ashford, Kent TN23 1AA (GB).</p> <p>(74) Agent: DEKKER, Enno, E., J.; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).</p> <p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
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<p>(54) Title: PERFUMED LAUNDRY DETERGENT POWDERS</p> <p>(57) Abstract</p> <p>The invention concerns perfumed, free flowing concentrated laundry detergent powders (concentrates), having a ratio of total solid constituents to total liquid constituents of less than 30:1, wherein the perfume is sorbed onto carrier particles which release at least 60 % w/w of the perfume in the Perfume Release Test and which are inert as defined by the Perfume Stability Test. The invention also concerns perfume-on-carrier systems designed for perfuming free flowing concentrated laundry detergent powders. Preferably the carrier particles are inorganic and have a perfume content of at least 25 % w/w.</p>															

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Perfumed Laundry Detergent Powders

Field of the Invention

The invention relates to perfumed laundry detergent powders 5 and to perfume-on-carrier systems for incorporation into laundry detergent powders.

Background of the Invention

Detergent powders for laundry use span a wide range of 10 compositions. Traditional (or "regular") products are typified by a detergent surfactant level of between 8% and 20% by weight in total, more commonly 10% to 15%. The surfactants may be anionic, non-ionic, cationic, zwitterionic or amphoteric in nature, and commercial 15 products may contain all classes of surfactants, but the predominant form is generally anionic (i.e. anionic surfactants typically account for 50% or more of the total surfactants). Typical detergent surfactants are described in detail in "Surfactant Surface Agents and Detergents", 20 volume II by Schwartz, Perry and Birch, Interscience Publishers (1958). The remainder of a laundry detergent composition generally comprises builders, fillers, moisture, soil release and soil suspension and anti-redeposition agents, and other optional adjuncts such as 25 processing aids, optical brighteners, dyes, foam control agents, anti-corrosion agents, perfumes, pH control agents, enzymes, stabilisers, bleaches and bleach activators. The level of solid components in regular laundry detergent compositions is high, usually above 75%, often above 85%. 30 Perfume loadings for such compositions are generally within the range 0.05% to 0.4%, more commonly 0.1% to 0.3%, and the ratio of solid constituents to organic liquid constituents in a regular detergent composition is usually at least 30:1, and is likely in practice to be considerably 35 higher, e.g. at least 150:1 and up to 500:1.

Laundry detergent powder concentrates and hyperconcentrates

(for the purposes of this specification further referred to as "concentrates") represent a relatively new product segment which is assuming increasing commercial importance world-wide. These concentrated products have a rather 5 different composition to that described above.

The total level of detergent surfactants in concentrates generally lies within the range 15% to 60% by weight of the powder, more usually 20% to 40%. In addition to the 10 difference in the level of surfactants another major point of difference concerns the level of low-functionality materials such as fillers. In concentrates the level of sodium sulphate for example, is rarely above 6% or even 2% by weight, whereas in regular powders levels of 20% to 30% 15 are common. The composition of the actives may be similar to that in regular products, i.e. predominantly anionics, but not restricted to this and, for example, a high proportion of non-ionics may be used advantageously. The use of higher proportions of non-ionic surfactants is 20 reported to be a significant trend in the detergent industry, at least for Europe, as reported by Smulders and Krings (Chemistry and Industry, March 1990, pages 160 to 163). Examples of detergent powder formulations with high 25 non-ionics levels are disclosed in EP 228011, EP 168102, EP 425277, and EP 120492. Many non-ionic surfactants are liquid at ambient temperatures. Yet another difference between "regulars" and concentrates is that the percentage of perfume incorporated into concentrates tends to be higher than that for regular powder use, and lies generally 30 above 0.1% by weight, normally within the range 0.4% to 2.5% by weight of the powder, more typically 0.5% to 1.5%.

Thus a concentrate may be defined for the purposes of the present specification as comprising at least 15% (and 35 preferably at least 20%) w/w total surfactant actives and at least 0.1% w/w perfume, preferably at least 0.4% w/w. A consequence of these differences between regulars and

concentrates is that the ratio of total solid to total organic liquid components for certain concentrates may be less than 30:1, or even less than 10:1, and problems can arise in manufacture and storage of the product due to

- 5 "stickiness" and lump formation. In particular, for concentrates incorporating relatively high levels of liquid non-ionic surfactants, processing problems may arise from agglomeration of particles, with handling difficulties during production, and with the possibility of forming
- 10 large powder conglomerates which are unacceptable to the end user of the product. Even after optimisation of the powder formulation it may be found that the addition of further liquid components such as perfumes to these systems will exacerbate the tendency for particle cohesion and
- 15 agglomeration, especially when the perfume is post-dosed into base powder, and when high levels of perfume are incorporated.

The prior art literature provides many instances where

- 20 perfume is delivered via the use of a solid carrier, which may be either organic or inorganic in nature, or both.

GB 2066839 discloses detergent powders containing perfume sorbed onto a porous carrier at a level of 10% to 65% by

- 25 weight. The carrier is a large surface area sorbent selected from a wide variety of substrates such as polyacrylates, polyvinyl chloride, urea-formaldehyde resins, polystyrene, hydrated silicon dioxide, titanium dioxide, aluminium trioxide, or mixtures thereof. The
- 30 primary objective of the invention disclosed therein is to decrease perfume losses through volatilisation and chemical attack during storage of perfumed powder products.

GB 1306924 describes perfume particles in free-flowing

- 35 powder form" prepared from perfume and a particulate silica, or more particularly from a mixture of a finely divided silica and an absorbent silica gel. The fragrance

loading in these particles may be as high as 70%. Manufacture is economical and involves simple mixing of perfume oil with the silicas, followed by sieving. Examples are disclosed of perfume particles suitable for use in 5 talcum powders, scouring powders, deodorants, toilet blocks, bath crystals and foot powders. No disclosure is made of use in detergent powders, and nothing is revealed regarding perfume stability within concentrates, nor are specific physical properties such as hydrophilic character 10 or bulk density disclosed.

US 4209417 teaches the use of perfume particles prepared using a water-soluble polymer together with an emulsifier. The loading of perfume in these particles may be high (30% 15 to 70%), but the manufacturing process involves drying large volumes of aqueous dispersions, with adverse consequences for throughput and economy. In addition, the perfume must be water-insoluble. The teachings of GB 2090278 are similar, except that the perfumed particle 20 contains water but is rendered free flowing by the inclusion of excess powdered hydratable material such as anhydrous alkali metal salts. The maximum possible loading of perfume is thereby significantly reduced.

25 Perfume-on-carrier systems for laundry detergent compositions as disclosed in EP 334666 are designed to deliver perfume to fabric efficiently through the use of fabric substantive carriers such as selected solid non-ionic or cationic surfactants. The processing involves melt 30 blending the components followed by spray chilling, and the resulting perfume loading is likely to be low (25% w/w or less). Similar targeted delivery of perfume is provided by the microcapsules described in EP 376385, where a complex coacervate prepared from perfume and polycationic and 35 polyanionic materials is coated with a water-insoluble cationic fabric softener which facilitates perfume delivery to fabric. In both these inventions the cost of manufacture

is relatively high and relatively complicated processing steps are involved.

5 GB 2140820 and GB 2141730 describe perfume-on-carrier systems based on zeolites or clays, with an optional coating of a fabric-adhesive agent, wherein the perfume loading in these carriers is low (10% or less). The carrier systems are designed to deliver perfume to fabric via the zeolite or clay, which are likely to contact fabric and be
10 dispersed thereupon during laundering, and are hydrophobic enough to retain sufficient perfume even in the wash solution.

15 EP 332259 and EP 332260 detail the use of silica perfume carriers in detergent powders and fabric softeners, respectively. The silicas span a wide range of types, with particle size of from 0.001 micron (fumed silica) through to 15 micron (silica gel), with a surface area of 100 - 800 m²/g. For laundry detergent powders the preferred silica is
20 a fumed type, with particle size in the range 0.007 micron to 0.025 micron, although silica gels may also be used, the preferred particle size being 1 to 8 micron. These silica carriers are optimised for application in detergent compositions providing perfume at a level of 0.01 to 0.5%,
25 and where the perfume includes components which require protection from hostile bleaching agents present in the detergent composition. The detergent compositions contain preferably 10% to 25% of detergentsurfactants. The examples given are high in anionic type surfactants, and
30 have high solid to organic liquid ratios. It is stated in EP 332259 that "in addition to separating and protecting the perfume from the bleach, it is believed that the silica particles deposit on fabrics and enhance the delivery of the perfume to the fabrics".

35

Summary of the Invention

It is the purpose of the present invention to provide a

method for incorporating perfumes in particulate form into concentrates so as to not adversely affect the flow properties of the detergent powder by the addition of perfume. It is another purpose of the invention to provide 5 perfume-on-carrier systems for incorporation into concentrates in which perfumes retain their integrity and which can release substantially all their fragrance to the wash liquor during conventional laundering.

10 Detailed description of the invention

In one aspect the invention provides perfumed, free flowing concentrated laundry detergent powders (concentrates), having a ratio of total solid constituents to total liquid constituents of less than 30:1 and containing at least 0.1 15 w/w of perfume, wherein the perfume is sorbed onto carrier particles which release at least 60% w/w of the perfume in the Perfume Release Test as described herein below and which are inert as defined by the Perfume Stability Test described herein below.

20

In another aspect the invention provides perfume-on-carrier systems wherein the carrier particles release at least 60% w/w of the perfume in the Perfume Release Test as described herein below and are inert as defined by the 25 Perfume Stability Test described herein below.

For the purposes of this invention a concentrated laundry detergent powder (or "concentrate") is defined as a detergent powder comprising:

30 - at least 15% w/w, preferably at least 20% w/w, more preferably between 20 and 60% w/w of detergent surfactants (for brevity hereinafter referred to as "surfactants").

- less than 10% w/w, preferably less than 6% w/w, more 35 preferably less than 2% of fillers, such as sodium sulphate.

Furthermore concentrates preferably have a bulk-density of

at least 600 g/l.

Finally, concentrates generally contain other components, such as builders (phosphates such as sodium tripolyphosphate, zeolites or NTA), soil suspension and anti-redeposition agents, enzymes, optical brighteners, processing aids, dyes, foam control agents, anti-corrosion agents, pH control agents, stabilisers. Bleaching detergents also contain bleaches and bleach activators.

10

The invention is particularly concerned with concentrates in which a substantial proportion, i.e. 35% w/w or more, of the surfactants is liquid at ambient temperature. In this respect it should be taken into account that in many cases 15 a particular surfactant is in fact a mixture of chemically closely related but slightly different components, e.g. a mixture of polymers with varying degrees of polymerization. Therefore, such products do not have a sharp melting point. For the purposes of this invention a surfactant is 20 considered liquid when at a temperature of 25°C and above it contains no more than 50% solids.

Under this definition the vast majority of anionic, cationic, zwitterionic and amphoteric surfactants are 25 solids and surfactants falling in the category of liquids are predominantly nonionics, although many other nonionics are solids.

The invention is therefore also particularly concerned with 30 concentrates in which a substantial part of the surfactant is of the nonionic type. In one embodiment it is concerned with concentrates comprising mainly nonionic and anionic surfactants in which the ratio of nonionic to anionic surfactant is at least 3:2 and wherein at least 35% w/w of 35 the total quantity of surfactants is liquid. Thus, in these concentrates generally at least 60% w/w of the nonionics is liquid. In another embodiment it is concerned with

concentrates in which all of the surfactants are nonionics, of which at least 35% w/w is liquid.

The concentrates according to the invention contain the 5 perfume-on-carrier systems according to the invention in a quantity to give at least 0.1% w/w (calculated on the total concentrate) of perfume in the concentrate, preferably 0.4-2.5% of perfume, more preferably 0.5-1.5% w/w of perfume in the concentrate. The actual quantity of perfume-on-carrier 10 system to be added thus also depends on the perfume content in the perfume-on-carrier system as hereinbelow described.

As used herein the term "perfume" denotes a substantially water-insoluble composition of matter consisting of one or 15 more perfume components, optionally mixed with a suitable solvent or diluent, which is used to impart a desired odour to the detergent product to which it is added and/or to the wash liquor, the skin, hair or the fabric.

20 Perfume components are those constituents of a perfume which are added thereto only or primarily for their olfactive contribution. Perfume components may be natural products such as extracts, essential oils, absolutes, resinoids, resins, concretes etc., but also synthetic 25 materials such as hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, esters, acetals, ketals, nitriles, etc., including saturated and unsaturated compounds, aliphatic, carbocyclic and heterocyclic compounds. Such perfume components are mentioned, for example, in S. 30 Arctander, Perfume and Flavor Chemicals (Montclair, N.J., 1969), in S. Arctander, Perfume and Flavor Materials of Natural Origin (Elizabeth, N.J., 1960) and in "Flavor and Fragrance Materials - 1991", Allured Publishing Co. Wheaton, Ill. USA.

35 Examples of perfume components are: geraniol, geranyl acetate, linalol, linalyl acetate, tetrahydrolinalol,

citronellol, citronellyl acetate, dihydromyrcenol, dihydro-myrcenyl acetate, tetrahydromyrcenol, terpineol, terpinyl acetate, nopol, nopyl acetate, 2-phenylethanol, 2-phenyl-ethyl acetate, benzyl alcohol, benzyl acetate, benzyl 5 salicylate, styrallyl acetate, benzyl benzoate, amyl salicylate, dimethylbenzyl carbinol, trichloromethylphenyl-carbonyl acetate, p-tert-butyl cyclohexyl acetate, isononyl acetate, vetiveryl acetate, vetiverol, α -hexylcinnam-aldehyde, 2-methyl-3-(p-tert-butylphenyl)propanal, 10 2-methyl-3-(p-isopropylphenyl)propanal, 3-(p-tert-butyl-phenyl)-propanal, tricyclodeceny1 acetate, tricyclodeceny1 propionate, 4-(4-hydroxy-4-methyl-pentyl)-3-cyclohexene-carbaldehyde, 4-(4-methyl-3-pentenyl)-3-cyclohexene-carbaldehyde, 4-acetoxy-3-pentyltetrahydropyran, 15 3-carboxymethyl-2-pentylcyclopentane, 2-n-heptylcyclo-pentanone, 3-methyl-2-pentyl-2-cyclopentenone, n-decanal, n-dodecanal, 9-decenol-1, phenoxyethyl isobutyrate, phenyl-acetaldehyde dimethylacetal, phenylacetaldehyde diethyl-acetal, geranyl nitrile, citronellyl nitrile, cedryl 20 acetate, 3-isocamphylcyclohexanol, cedryl methyl ether, isolongifolanone, aubepine nitrile, aubepine, heliotropin, coumarin, eugenol, vanillin, diphenyl oxide, hydroxy-citronellal, ionones, methylionones, isomethylionones, irones, cis-3-hexenol and esters thereof, indan musks 25 tetralin musks isochroman musks macrocyclic ketones, macrolactone musks ethylene brassylate, aromatic nitromusks.

30 Suitable solvents and diluents for perfumes as mentioned above are, for example, diethyl phthalate, triethyl citrate, ethanol, isopropanol, dipropylene glycol, etc.

35 The perfume-on-carrier systems (hereinafter for brevity referred to as "POC systems") according to the invention comprise a perfume as defined above and an inert particulate carrier. Inertness of the carrier is tested with a test perfume as described below in the "Perfume

Stability Test". For the purposes of this invention a carrier is considered inert if each component in the test perfume 1 of Table 1 below suffers no more than 5% deterioration under the test conditions.

5

Also the POC systems should easily release a substantial proportion of its perfume content when immersed in a laundry wash liquor. This ability requires the carrier to be sufficiently hydrophobic and the suitability of a

10 carrier can be determined with the "Perfume Release Test" described below. For the purposes of this invention a carrier is considered to pass the test if under the test conditions it is found to release at least 60% of the test perfume 2 of Table 2 below.

15

The POC systems comprise preferably at least 25% w/w of perfume, more preferably at least 40% and most preferably at least 70% w/w. Yet the POC system should remain free-flowing.

20

Conveniently the inert carrier particles have a mean diameter in the range 5-50 microns, preferably in the range 10-50 microns, more preferably in the range 15-50 microns, most preferably in the range 20-50 microns. Also, they should preferably have a surface area in the range 100-450 m²/g, more preferably in the range 100-350m²/g, most preferably in the range 100-300 m²/g. Preferably an inorganic carrier is used, such as a silica, zeolite or clay. Typically the carrier particles are of amorphous silica.

30 In addition to the POC system the concentrates according to the invention may comprise up to 20% w/w of the total perfume quantity, and preferably no more than 10%, in 35 microencapsulated form (e.g. as spray dried starch encapsulates).

The POC systems are conveniently prepared by mixing the perfume with the carrier particles. The mixing of the perfume and the carrier may be carried out in a variety of ways known to the practitioner in the art, for example by 5 spraying the perfume onto the particles contained in a rotary drum or positioned on a conveyor belt. A non-limiting example of a suitable procedure involves the use of a Tatham-Forberg mixer in a low speed, short duration operation. The equipment comprises a twin-drum assembly 10 with a rotary twin-shaft arrangement. Attached to each shaft is a set of carefully profiled paddles positioned at specific angles. The powder charge is fluidised by the paddle rotation and the perfume oil is sprayed on and mixing is continued until perfume take up is complete. The 15 perfumed particle mass is then dropped through the bottom of the mixer into a suitable container.

Absorption or adsorption of perfumes into or onto inert carrier particles will not necessarily protect the perfumes 20 against attack by bleaching compounds. Thus, for use in concentrate formulations containing bleaching agents (which are particularly hostile to perfume components) the perfume is preferably one which is resistant to such attack and retains high performance even when stored in the presence 25 of such hostile ingredients. Suitable non-limiting examples are disclosed in EP 299561 and US 4663068.

The POC systems of the present invention may be incorporated into concentrates using standard powder 30 handling equipment, known in the art, e.g. by utilisation of weigh-belts.

Concentrate formulation Examples

High non-ionic surfactant content concentrates within the 35 scope of application defined herein are detailed in the references cited above, and two examples are shown below in Tables I and II.

Table I

CONCENTRATE "A"		% w/w
	Zeolite 4A	33.2
5	Sodium carbonate	11.2
	Dobanol 23-3	12.1
	Dobanol 23-6.5	10.2
	Sodium LAS	6.2
	Sodium sulphate	3.8
10	Polyacrylate (mw 3000-4000)	3.5
	Sodium silicate	1.9
	Sodium soap	2.6
	POC system particles	2.0
	Enzymes	1.3
15	Anti-redeposition agent	0.9
	Antifoam	0.4
	Sodium EDTA	0.4
	Water, dye, minor components	10.3
20		100

Table II

CONCENTRATE "B"		% w/w
5	Zeolite 4A	29.8
	Sodium perborate*	15.6
	Sodium carbonate	9.7
	TAED granules **	8.2
10	Dobanol 23-3	8.7
	Dobanol 23-6.5	7.3
	Sodium LAS	5.1
	Polyacrylate (mw 3000-4000)	3.1
	Sodium sulphate	1.6
	POC system particles	1.2
15	Sodium soap	1.5
	Sodium silicate	1.5
	Enzymes	0.8
	Anti-redeposition agent	0.4
	Sodium EDTA	0.3
20	Antifoam	0.3
	Water, dye, minor components	4.9
		100
	* monohydrate	
25	** tetraacetalythylene diamine sodium salt	

Perfume Stability Test

A particulate sample (2g) was prepared by incorporating 20% of the perfume test mixture 1 detailed in Table 1 into an 5 inorganic carrier under evaluation. The sample was stored in glass vials (10ml) for one week at 37°C prior to analysis. The vials were tightly sealed and free movement of air throughout the test system was minimised by packing the free headspace volume with cotton wool.

10

Analysis was carried out by extraction of the sample using ethyl acetate, followed by determination of the residual mass of the indicator materials using standard gas chromatographic techniques.

15

Suitable carriers according to this test are those for which each of the indicator materials suffer no more than 5% degradation (i.e. each component in the system displays at least 95% stability). Such carriers are defined as 20 passing the Perfume Stability Test for the purposes of the present application.

Table 1: Perfume Test Mixture 1

25	Material	w/w%
	Benzyl acetate	25
	Limonene	25
	Tetrahydrolinalol	25
	Inert internal standard*	25
30	* e.g. Tetradecane	

Perfume Loading

Equal amounts of carrier material were placed in a series of glass vials and various aliquots of a mixture of perfume

components were added (Perfume Test Mixture 2 as shown in Table 2). Each carrier/perfume system was agitated with a spatula, sealed in the vial and stored at ambient temperature for 24 hours prior to inspection. "Perfume 5 Loading" was taken as the loading at which the perfume-on-carrier mixture ceased to flow easily as judged by eye.

Table 2: Perfume Test Mixture 2

	Material	w/w%
10	Benzyl acetate	20
	Hexylcinnamic aldehyde	20
	PTBCHA	20
	Tetrahydrolinalol	20
15	Tonalid	20

KEY: "Tonalid" is a trademark for 1,1,2,4,4,7-hexamethyl-6-acetyl-1,2,3,4-tetrahydronaphthalene
 "PTBCHA" is 4-tert.butylcyclohexyl acetate

20 Perfume Release Test
 The POC system under evaluation (containing at least 20% by weight of Perfume Test Mixture 2, Table 2) were equilibrated for 3 days and then added at ambient 25 temperature to an aqueous model wash liquor at a level yielding a theoretical maximum perfume concentration of 40 ppm. The wash liquor (10g) comprised ca. 0.05% of a mixture of a non-ionic surfactant (Dobanol 25TM, a mixture of ethoxylated fatty alcohols with an average of 7 ethoxyl 30 groups) and an anionic surfactant (sodium lauryl sulphate) in a weight ratio of 2.3 to 1.

The mixture was shaken for 10 seconds and immediately placed in a centrifuge and spun for 5 minutes at 2000 RPM.

The bulk of the supernatant liquid was withdrawn (ca. 95% by weight of the aqueous phase, measured accurately) and filtered prior to extraction with ethyl acetate (10g, containing hexadecane as an internal standard). The ethyl 5 acetate was obtained by centrifugation and was analysed by gas chromatography. The amount of perfume released into the aqueous phase was then calculated.

A perfume release efficiency of 60% or over is taken as 10 indicative of bulk release of the perfume under actual wash conditions where temperatures of 35°C to 65°C or higher are common, and longer wash times are likely (e.g. 15-30 minutes, or longer in a soak regime). Carrier materials achieving this are considered to pass the Perfume Release 15 Test.

Carrier material test examples

A range of commercial inorganic particles was subjected to the above tests. The results of these tests together with other relevant data are shown in Tables 3 and 4. It can be
 5 seen that the two precipitated silicas meet the criteria specified above, Neosyl GPTM and HP 39TM.

Table 3

	Carrier	Surface Area m ² /g	Mean Particle Size micron	Perfume Loading % w/w	Stability		
					BA	Lim	THL
10	Gasil 200*	750	4.6	20	95	90	100
	Neosyl GP*	200	18	65	95	95	95
15	Aerosil 200**	200	0.01	80	100	90	100
	Zeolite 4A*	-	-	30	85	85	100
20	Gasil EBN*	320	9	55	100	85	100
	HP39*	300	11	65	95	95	95
25	Aerosil 300**	300	0.01	75	95	90	100
	Neosyl LD*	>400	12	25	90	95	100

Key: BA-Benzyl acetate Lim-Limonene THL-tetrahydrolinalol
 (i.e. the perfume components of Perfume Test Mixture 1)

* Available from Crosfield Group, weight mean particle size determined using Malvern particlesizer

5 ** Available from Degussa, average primary size obtained from electron microscopy, surface area determined by the BET method

10 + trade mark substances available from Linde division, Union Carbide

10

Table 4 Perfume Release

Carrier	% Perfume released
Aerosil 200**	52
15 Aerosil R812**	42
Gasil 200**	20
HP39*	70
Neosyl GP*	68

Key: */** as for Table 4

20

Application Example 1

POC system particles containing 50% perfume were prepared from Neosyl GPTM and fragrance "A" as specified in Table 5.

25 These were incorporated into concentrate powder (formulation A, Table 1) at a level of 1.1% to yield a perfume loading of 0.55%. The powder was stored in domestic laminated cardboard containers at 37°C/70% RH (relative humidity) for 4 weeks and examined. No adverse effect was 30 noted on powder flow properties.

Application Example 2

POC system particles containing 50% perfume were prepared from Neosyl GPTM and fragrance "A" as specified in Table 5.

These were incorporated into a concentrate powder (formulation B, Table 1) at a level of 1.1% to yield a perfume loading of 0.55%. The powder was stored in domestic laminated carboard containers at 37°C/70% RH (relative 5 humidity) for 4 weeks and examined. No adverse effect was noted on powder flow properties.

Application Example 3

POC system particles containing 55% perfume were prepared 10 were prepared from Neosyl GPTM and fragrance "B" as specified in Table 6. These were incorporated into a concentrate powder (formulation B, Table 1) at a level of 1.45% to yield a perfume loading of 0.8%. The powder was stored in domestic laminated cardboard containers at 15 37°C/70% RH for 4 weeks and examined. No adverse effects was noted on powder flow properties.

Application Example 4

POC system particles containing 55% perfume were prepared 20 from HP 39TM and fragrance "B" as specified in Table 6. These were incorporated into a concentrate powder (formulation B, Table 1) at a level of 1.45% to yield a perfume loading of 0.8%. The powder was stored in domestic laminated carboard containers at 37°C/70% RH for 4 weeks 25 and examined. No adverse effect was noted on powder flow properties.

Application Example 5

A starch encapsulate was prepared containing 40% perfume 30 oil. The starch was a modified waxy maize starch (CapsulTM, National Starch) and the perfume was a freshness accord (Fragrance C, Table 7) of perfume materials susceptible to attack by bleach components in laundry powder. The encapsulate was prepared by normal spray-drying procedures, 35 well known to those experience in the art. An emulsion of 40% starch in water was prepared and sufficient perfume added to constitute 40% of the total of starch and perfume.

This emulsion was then spray-dried using a conventional spray-dryer (Niro Mobile Minor) with rotary atomizer, inlet temperature 240°C, outlet temperature 100°C.

- 5 POC system particles containing 50% perfume were prepared from Neosyl GPTM and fragrance "B" (see Table 6). These were mixed into a concentrate powder (formulation B, Table 1) at a level of 1.1% to yield a perfume loading of 0.55%. To this product was then mixed in 0.2% of the starch
- 10 encapsulate detailed above, yielding an overall perfume level of 0.63%. The powder was stored in domestic laminated cardboard containers at 37°C/70% RH for 4 weeks and examined. No adverse effect was noted on powder flow properties.

Table 5 Formulation of fragrance "A"

Material	Quantity %
Anther (Q)	1.0
Coumarin	2.0
Gyrane (Q)	0,5
Hexyl cinnamic aldehyde	18.0
Jasmacyclene (Q)	5.0
Jasmopyrane Forte (Q)	4.0
Lilial (G)	10.0
Lixetone (Q)	8.0
Methyl ionone alpha iso (Q)	5.0
4-tert.butylcyclohexyl acetate (Q)	5.0
2-Phenylethyl alcohol	15.0
Pivacyclene (Q)	0.5
Tetrahydrolinalol	6.0
Traseolide (Q)	20.0

Q: trade mark material available from Quest

G: trade mark material available from Givaudan

Table 6 Formulation of fragrance "B"

	Material	Quantity %
	Dimethylbenzyl carbonyl acetate	15.0
	4-tert.butylcyclohexyl acetate (Q)	17.5
5	Tetrahydrolinalol	15.0
	Anther (Q)	3.5
	Traseolide (Q)	5.0
	Decanol	5.0
	Phenylpropanol	6.0
10	Herboxane	10.0
	Diphenylmethane	5.0
	Cedramber (IFF)	4.0
	Hexadecanolide	5.0
	2-Phenylethyl alcohol	6.0
15	Dihydroterpineol	3.0

Q: trade mark material available from Quest

IFF: trade mark material available from IFF

Table 7 Formulation of fragrance "C"

Material	Quantity %
Adoxal (G)	1.0
Aldehyde C9 50% in DEP	7.0
Aldehyde C10 50% in DEP	16.0
Aldehyde C11 (undecylenic) 50% in DEP	30.0
Aldehyde C12 50% in DEP	10.0
Methyl nonyl acetaldehyde 50% in DEP	36.0

10 G: trade mark material supplied by Givaudan

DEP: diethylphthalate (diluent)

CLAIMS

1. A perfumed, free flowing concentrated laundry detergent powder comprising:
 - 5 - at least 15% w/w of detergent surfactants,
 - less than 10% w/w of fillers, having a ratio of total solid constituents to total liquid constituents of less than 30:1 and containing at least 0.1% w/w of perfume, wherein the perfume is
 - 10 sorbed onto carrier particles which release at least 60% of the perfume in the Perfume Release Test as described herein and which are inert as defined by the Perfume Stability Test as described herein.
- 15 2 A detergent powder according to claim 1, having a bulk density of at least 600 g/l
3. A detergent powder according to claim 1 or 2 wherein the amount of detergent surfactant is at least 20% w/w and the amount of filler is less than 6% w/w
- 20 4. A detergent powder according to any one of the preceding claims, wherein at least 35% w/w of the surfactants are liquids as herein defined.
- 25 5 A detergent powder according to claim 4 comprising nonionic and anionic detergent surfactants wherein the ratio of nonionic detergent surfactants to anionic detergent surfactants is at least 3:2 and at least 60% w/w of the nonionic detergent surfactants is liquid
- 30 6. A detergent powder according to claim 4 wherein all detergent surfactants are nonionic of which at least 35% are liquid

7. A detergent powder according to any one of the preceding claims wherein the carrier particles are inorganic and carry at least 25% w/w of perfume .
- 5 8. A detergent powder according to claim 7 wherein the carrier particles carry at least 40% w/w of perfume .
9. A detergent powder according to claim 7 or 8 wherein the carrier particles have a mean diameter in the 10 range of 5-50 microns.
10. A detergent powder according to claim 9 wherein the carrier particles have a mean diameter in the range 10-50 microns.
- 15 11. A detergent powder according to any one of claims 7-10, wherein the carrier particles have a surface area in the range 100-450m² /gram.
- 20 12. A detergent powder according to claim 11, wherein the carrier particles have a surface area in the range 100-350m² /gram.
13. A detergent powder according to any one of claims 7-12 25 wherein the carrier particles are of amorphous silica.
14. A perfume-on-carrier system wherein the carrier particles release at least 60% w/w of the perfume in the Perfume Release Test as described herein and are 30 inert as defined by the Perfume Stability Test described herein.
15. A perfume-on-carrier system according to claim 14 wherein the carrier particles are inorganic and carry 35 at least 25% w/w of perfume .

16. A perfume-on-carrier system according to claim 15 wherein the carrier particles carry at least 40% w/w of perfume .
- 5 17. A perfume-on-carrier system according to claims 15 or 16 wherein the carrier particles have a mean diameter in the range of 5-50 microns.
- 10 18. A perfume-on-carrier system according to claim 17 wherein the carrier particles have a mean diameter in the range 10-50 microns.
- 15 19. A perfume-on-carrier system according to any one of claims 15-18, wherein the carrier particles have a surface area in the range 100-450m² /gram.
- 20 20. A perfume-on-carrier system according to claim 19, wherein the carrier particles have a surface area in the range 100-350m² /gram.
21. A perfume-on-carrier system according to any one of claims 15-20 wherein the carrier particles are of amorphous silica.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 93/03695

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C11D3/50 C11D17/00 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 325 457 (KAO CORPORATION) 26 July 1989 see page 2, line 55 - page 5, line 12; examples 1-5 ---	1-3,14
X	EP,A,0 478 326 (QUEST INTERNATIONAL B. V.) 1 April 1992 see column 2, line 8 - column 4, line 46; examples 1,2,13 ---	14-18,21
X	EP,A,0 334 490 (INTERNATIONAL FLAVORS & FRAGRANCES INC.) 27 September 1989 see page 9, line 14 - page 9, line 45 see page 12, line 30 - page 14, line 16 ---	14 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

1 Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 93/03695

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 115, no. 6, 12 August 1991, Columbus, Ohio, US; abstract no. 52294m, KIYOSHI MIZUNO 'Granular laundry detergent compositions having high bulk density and containing perfumes for fabrics' page 148 ; see abstract & JP,A,03 035 100 (LION CORP.) 15 February 1991 -----</p>	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/03695

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EP-A-0325457	26-07-89	JP-A-	1185399	24-07-89
		JP-A-	1193397	03-08-89
		US-A-	4992198	12-02-91
EP-A-0478326	01-04-92	JP-A-	4265149	21-09-92
		US-A-	5185155	09-02-93
EP-A-0334490	27-09-89	US-A-	4842761	27-06-89
JP-A-03035100	15-02-91	NONE		